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Methods for the Preparation of Initiating and Delay Compositions

G. W. C. Taylor

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CRYSTALLISATION PANEL  
OF THE  
PHYSICAL AND INORGANIC CHEMISTRY COMMITTEE

(MUNITIONS CHEMISTRY ADVISORY BOARD)

Methods for the preparation of initiating and delay compositions  
by  
G.W.C. Taylor

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MINISTRY OF SUPPLY

Explosives Research and Development Establishment

E.R.D.E. Report No. 30/R/48

✓ Methods for the Preparation of Initiating and Delay Compositions

by

G.W.C. Taylor

This report does not contain information of overseas origin.

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November 1948

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## SUMMARY

### Object of Investigation

This report supplements C.R.D.D. Technical Memorandum No. 1/M/47 "Crystallisation Problems in the Development of New and Improved Initiating and Delay Compositions." It gives examples of investigations to provide required physical properties by controlling crystal formation and growth and by surface treatment and deposition in these classes of explosives.

### Scope of Investigation

Methods described can be classified:-

1. Control of particle size and shape by indirect crystallisation i.e. through an intermediate crystalline substance not isolated in the process.
2. Control of crystallisation by the use of additive substances affecting nucleation but not included in the final product.
3. Nucleation by additive substance retained in the crystals of the product.
4. Precipitation in the presence of hydrophilic colloids.
5. Employment of a proportion of the explosive as a colloid.
6. Deposition and surface treatment - reproduction of mechanical mixtures.

These methods have been first studied in the laboratory to meet Service or experimental requirements for compositions with suitable physical and explosive characteristics e.g. flowing properties, ignitability, rate of burning. Promising processes have then been developed to the manufacturing scale.

The substances investigated include lead azide, lead styphnate, barium styphnate, lead 2:4 dinitroresorcinato, lead 4:6 dinitroresorcinato. Examples are given from manufacturing processes and from investigations in progress.

### Conclusions

The results illustrate the very wide range of modification of physical and explosive properties which may be attained using the methods described and with a comparatively small number of substances. This is important as there are few substances in this class which possess suitable explosive properties combined with adequate stability and compatibility. Attention should be drawn to the effect on crystal growth of very small proportions of additive substances, in particular the non-ionic surface active agents; dilution of explosive properties is thereby almost entirely eliminated. This can be compared with co-precipitation with hydrophilic colloids which can also be employed at small proportions.

The enhanced sensitiveness of crystallising substances to the presence of impurities during polymorphic transition or changes in basicity or degree of hydration is repeatedly shown but is not always essential for desired crystal modification by co-precipitation.

Some examples show that surface condition can be more important than the shape of the crystal in obtaining satisfactory flowing properties for machine-filling.

### Recommendations

In continuing the investigations outlined in this report it is suggested

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that the following should receive attention:-

(1) Extending the studies of crystal formation and growth and surface treatment to include substances not necessarily of potential explosive application but with similar crystal characteristics to those described. The objective would be to obtain more general data to correlate experimental results.

(2) The most promising fields are in the employment of surface active substances both non-ionic and ionic types for modifying crystallisation without incorporation and also for surface treatment to improve flowing properties and stability.

(3) Only a small beginning has been made in trying to eliminate the many complex mechanical mixtures in common use and it is considered that the methods of co-precipitation and deposition described could be more widely applied to give homogeneous non-segregating compositions.

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REPORT

Introduction and objects

New and improved initiatory and delay compositions are demanded in order to meet the requirements of existing and projected explosives stores. The inception and development of such composition involves a study of the physical characteristics of possible substances in relation to any methods of preparation or modification which can be adopted. A satisfactory product must not only possess the required properties of ignition when in use in the fuze, detonator or other store but must also be suitable for consistent manufacture in a physical form applicable to filling factory practice. Initiators and fast burning delay compositions are usually sensitive explosives and practicable methods of preparation and processing are limited owing to the risk of accidental explosion. The final product must be stable to conditions of temperature and humidity encountered in Service use and also compatible with metals and any other materials with which it is required to be in contact.

The ideal composition is a single chemical substance which can be prepared simply on a manufacturing scale to give a consistent reproducible product meeting all filling and proof requirements. This ideal is rarely if ever attained and one result is the very frequent resort to the use of two or more component mechanical mixtures with the obvious attendant disadvantages; mechanical processing methods, such as corning, in order to provide free-flowing and non-segregating products are sometimes adopted but this cannot be considered to be a satisfactory solution particularly when sensitive explosives are involved.

Any investigation of possible substances for initiating or delay application soon discloses the very considerable influence of the physical form of the product on processing, handling and the eventual performance at proof test. The general procedure, therefore, is to study the results of controlling physical form by modifying methods of preparation keeping in mind the limitations imposed by the nature of the substance and manufacturing considerations. Many likely substances in this class of explosive are sparingly soluble salts and in a typical precipitation process it is possible to alter rate of formation of nuclei and growth of crystals in order to modify particle size and shape. This is achieved by adjusting main variants such as choice and concentrations and temperatures of reactants, pH of solutions, and rates of agitation and addition.

For a large number of potentially useful compositions however the conclusion of these experiments fails to secure a suitable and consistent product. For example the substance may crystallise persistently in an unsatisfactory form such as in acicular or lamellar habit resulting in a bulky and poor flowing material unsuitable for processing and handling. Alternatively the required burning or detonating properties may not have been attained or may have been shown to be critically dependent on small and uncontrollable differences in particle size and shape. In this connection a final particle or granule of approximately spherical shape (not necessarily composed of a single pure substance) would not only give a free-flowing composition but would also ensure random distribution on filling thus avoiding effects due to preferred orientation of the crystals under pressing load. The surface treatment of promising substances to modify flowing, burning or other physical properties represents a further stage in the attempt to meet requirements.

The investigation of methods of preparation to overcome the difficulties indicated and to achieve satisfactory manufacturing processes and products has been carried out over a number of years and it is possible to give collected examples of results obtained.



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This report therefore supplements C.R.D.D. Technical Memorandum No. 1/M/47 "Crystallisation Problems in the Development of New and Improved Initiating Compositions."

#### Methods employed and examples of results obtained

The methods and results can be classified under the headings:-

1. Control of particle size and shape by indirect crystallisation, i.e. through an intermediate crystalline substance not isolated in the process.
2. Control of crystallisation by the use of additive substances affecting nucleation but not included in the final product.
3. Nucleation by additive substance retained in the crystals of the product.
4. Precipitation in the presence of hydrophilic colloids.
5. Employment of a proportion of the explosive as a colloid.
6. Deposition and surface treatment - reproduction of mechanical mixtures.

#### (1) Control of particle size and shape by indirect crystallisation

Where direct crystallisation of the required substance results in a product of unsatisfactory crystal habit, particle size or degree of uniformity it is possible, with certain substances, to obtain substantial improvement in physical form by indirect crystallisation through an intermediate which is not isolated. The intermediate may consist of a salt of different basicity or state of hydration or other complex from the substance required. The conversion of the intermediate to the final product can frequently be closely controlled in a batch process to give a less common crystal habit or marked uniformity in crystal size.

For example barium styphnate (barium trinitroresorcinate monohydrate, monoclinic) crystallises as shown in Fig. 1 when prepared by the interaction of barium carbonate or barium acetate with styphnic acid. Different crystal habits can be obtained by using other solutions as shown in Figs. 2, 3 but these products are not randomly orientated when compressed into delay sleeves. This results in irregular rates of burning. A desirable but unfamiliar crystal habit is shown in Figs. 4, 5. This can be obtained by first precipitating the trihydrate by the addition of magnesium styphnate solution to barium acetate solution and maintaining above the transition temperature to convert to the monohydrate; this conversion is accelerated by the addition of nitric acid. The conversion from the acicular trihydrate to the required crystal habit is illustrated by Fig. 6. This process was developed to the manufacturing scale to give a product known as R.D.1320 giving consistent rates of burning in delay sleeves for fuzes.

As a further example lead styphnate (lead trinitroresorcinate monohydrate, monoclinic) can be obtained in required crystal habits and particle size by indirect crystallisation through "basic salts". These are basic salts in the sense that they have higher lead content than the normal salt. When lead acetate solution is added to magnesium styphnate solution opaque yellow micro-aggregates (Fig. 7) are first formed. This is an adsorption complex of indefinite composition which changes to lead aceto-styphnate in the form of acicular crystals (Fig. 8). By altering the conditions of precipitation either of these intermediates (or the true monobasic salt obtained at higher pH) can be converted by the addition of nitric acid to the normal lead styphnate. Conversion of the microaggregates is favourable to the

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equant crystal habit (Fig. 9); the lead aceto-styphnate conversion favours the flatter crystal habit (Fig. 10). Slow addition of nitric acid gives large crystals and increase in rate of addition gives progressively smaller crystals (Fig. 11). Intermediate stages of two preparations are shown in Figs. 12-16. These processes have been developed satisfactorily to the manufacturing scale for a general purpose dust-free lead styphnate of high bulk density (R.D.1302) and lead styphnate (R.D.1303) which will mix with powdered graphite without segregating to give an electric cap composition.

This method of indirect crystallisation therefore gives control in batch processes for both crystal habit and crystal size of the product.

(2) Control of crystallisation by the use of additive substances affecting nucleation but not included in the product

A distinction can be drawn between precipitation methods which depend upon the incorporation of a measurable proportion of additive substance and those which employ an additive substance to modify crystal formation and growth without being included in the final product. The theory of the factors influencing crystal growth have been studied by Gibbs, Curie and others and the work of Marc on the use of dyes for modifying crystallisation velocity can be quoted for examples where considerable changes in crystal habit are shown with relatively little adsorption of the foreign substance. The influence of urea on the crystallisation of sodium chloride is usually cited as the classical example. When a colloid is co-precipitated and incorporated in the product either the individual crystal becomes translucent or opaque and loses its crystalline facets or alternatively the colloid may function as a binding or aggregating medium for small crystals. When no appreciable incorporation or aggregation takes place the crystals retain their normal transparent appearance but may be modified in size and/or shape by the presence of an additive substance in the liquors.

This method has been studied for the preparation of initiating and fast delay compositions as it has the appreciable advantage of reducing the possibility of dilution of the explosive. As an example a considerable reduction in crystallisation velocity on certain faces is achieved with methyl cellulose for barium styphnate without any noticeable incorporation of the colloid (Fig. 17). Note also the crystal habit of barium styphnate crystallised from sodium carbonate and carboxy methyl cellulose (Fig. 18). With the same explosive the effect of a dye (methyl violet) was found to be relatively small. In the preparation of normal lead 2:4 dinitroresorcinate the addition of urea has given indication of promoting acicular crystal habit thus decreasing bulk density.

The class of substances generally described as surface active agents has been found in this Establishment to be particularly applicable as additives to modify crystals of initiatory explosives without inclusion. Anionic surface active agents usually form insoluble nuclei and will be mentioned in the next group of methods but the non-ionic type which are not reactive to most of the solutions employed have given results of interest. The results obtained from these investigations show that a very small addition of certain surface active agents can profoundly affect nucleation and subsequent crystal growth and may be particularly valuable for suppressing undesirable polymorphic forms.

For example pure lead azide precipitated by the interaction of lead acetate and sodium azide solutions is of irregular and irreproducible crystal growth and is usually a mixture of alpha (orthorhombic) and the less stable and undesirable beta (monoclinic) polymorphs. The respective effect of the addition of a water dispersible and a water soluble surface active agent compared with a control precipitation is shown in Figs. 19-24. The beta form can be entirely eliminated and uniform crystal growth produced. This

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process has been developed satisfactorily to the manufacturing scale. Virtually all the additive substance is retained in the mother liquor and the process therefore gives pure lead azide by a controllable method. The surface active agent also facilitates washing and filtering of the product.

As another example of a different type may be quoted the crystallisation of lead styphnate in the presence of a surface active agent in order to prepare the beta polymorph at higher temperature.

Investigations have also shown that the addition of very small proportions of surface active substances may be employed in order to improve flowing properties of the crystals, for example, barium styphnate can be improved by this method.

(3) Nucleation by additive substances retained in the crystals of the product

By the introduction of a small proportion of a less soluble substance in a finely divided condition marked control of crystal development can be obtained in a number of cases. The employment of an anionic surface active agent of the sulphonate type in the precipitation of lead azide is an example. The insoluble lead sulphonate is first precipitated in a very fine state of division, providing abundant nuclei for the lead azide crystal growth. The resultant product is therefore of extremely small crystal size as shown in Fig. 25.

A further example is in the manufacture of Service lead azide, about 2 per cent lead carbonate being precipitated in situ by the advance of lead acetate solution added to the base solution of sodium carbonate. The familiar orthorhombic crystals of lead azide when viewed between crossed nicols show clearly the two skeletal growths to each crystal of lead azide corresponding to the nuclei (Fig. 26).

An interesting point arose in the use of this method by the nucleation of barium styphnate with barium carbonate. Uniform crystal development was achieved but the burning properties of the explosive were markedly affected and the product was unsuitable as a delay composition. This may indicate that nucleation with an inert substance is more suitable for a detonating or priming composition.

By the simultaneous addition of solutions of lead acetate and sodium azide to a base solution of colloiddally dispersed graphite the graphite may be intimately incorporated in the growing lead azide crystals to give a completely opaque product with interesting properties. Adjustment of conditions can result in different crystal formations from the mainly rhombic to the dendritic aggregated types (Fig. 27). This product has been recently developed to the manufacturing scale.

(4) Precipitation in the presence of hydrophilic colloids

The adsorption of foreign substances by growing crystals is a common phenomenon with numerous references in the literature. Among technical applications the adoption of dextrin to give a less sensitive form of lead azide is well known. The possibility of using other colloids to modify physical form in a wider sense than that of desensitising has been examined in some detail in this establishment. For example it has been possible to prepare lead 2:4 dinitroresorcinate co-precipitated with a small proportion of high viscosity type methyl cellulose with a faster rate of burning than a control preparation without the colloid. Special attention has been paid to using small proportions of colloid with less than 1 per cent included in the product.

Improvement of flowing properties and modification of detonating or rate

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of burning characteristics are the two main contributions which can be made in the development of new compositions by co-precipitation in the presence of colloids. Examples can also be given where products of improved cohesive and adhesive properties have been made and colloids have been used to eliminate the effects of impurities in ingredients.

The precise mechanism of adsorption on growing crystals is still a matter of controversy and no definite rules can be formulated for the use of this method in order to obtain particular results. It is possible however to give a general account of the factors involved and some conclusions based upon hundreds of experiments using the substances indicated.

The first considerations are:-

- (a) Nature of substance to be precipitated or crystallised.
- (b) Selection of colloid.
- (c) General conditions of precipitation.
- (d) Proportion and method of use of the colloid.

The most simple case of crystallisation represents a large number of alternative conditions and with precipitations involving intermediate forms and solid phases the problem may be very complex. The solubility of the substance in the supernatant liquor and the rate of nuclei formation and crystal growth can usually be modified over a wide range by alteration of concentrations temperature, degree of agitation etc. in order to establish conditions favourable to the incorporation of the colloid.

The available hydrophilic colloids are substances of high molecular weight mostly obtained from animal or plant sources. They include the water-soluble proteins such as gelatin, the water-soluble gums such as gum arabic, and colloids of the type of sodium alginate; representatives of these groups have been investigated in the precipitation of initiators. As a class however the cellulose and starch derivatives offer distinct advantages. Many are available in reasonably pure and consistent supply from commercial sources. They cover a wide range of physical properties influencing crystallisation and their advantages and scope have been verified experimentally in this work. Methyl cellulose and carboxy methyl cellulose and also the starch glycollate derivatives are particularly valuable. They are water soluble over a considerable range of molecular weight and degree of substitution giving a correspondingly wide range of precipitation characteristics. Even at low concentrations highly viscous solutions are obtainable and this is reflected in the marked effect of very small quantities as additives. The presence of the glycollate side-chain in both cellulose and starch derivatives contributes considerably to the efficiency of these colloids as shown in the examples in this report.

The proportion of colloid should be kept to a minimum to avoid marked desensitisation and possible hygroscopicity of the product. A distinction must be made between the quantity of colloid used and the amount actually incorporated in the product; in some cases 10 per cent of the colloid has been added to reacting solutions to obtain less than 1 per cent incorporation. Mechanical conditions may be critical and for any series of co-precipitation experiments it has been necessary carefully to standardise the procedure.

A distinction should also be drawn between colloids which are included in the growing crystals without undergoing chemical change and those which are converted to another substance during the process. Methyl cellulose is

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not reactive chemically in the type of double decomposition precipitation commonly employed and is incorporated unchanged. Sodium cellulose glycollate (sodium carboxy methyl cellulose) however forms an insoluble lead salt in the presence of a soluble lead salt; this insoluble salt is the effective colloid and such preparations as granulated lead azide can be more correctly described as true co-precipitation.

Examples of products by this method

(a) Granulated barium styphnate (R.D.1320B). By adding a mixture of magnesium styphnate and sodium carboxy methyl cellulose solutions to a solution of barium chloride it is possible to obtain opaque almost spherical granules of barium styphnate markedly different from the crystals formed by normal methods of preparation (Fig. 28). This product contains only 0.7 per cent carboxy methyl cellulose. With reduced proportion of colloid a characteristic etched crystal type is produced (Fig. 29). X-ray diffraction examination confirms that the granular product is essentially the same substance and not a polymorphic form and the pattern of the granules corresponds to a small number of crystals of the order from one to six (Fig. 30); with increase in proportion of colloid the number of constituent crystals greatly increases. Granulated barium styphnate is a very stable substance and its method of preparation has been developed to the manufacturing scale.

(b) Granulated lead styphnate (R.D.1316). Lead styphnate in the form of free-flowing rounded granules can be prepared in a single stage process by the addition of lead nitrate solution to a stirred and heated mixture of magnesium styphnate and methyl cellulose solutions, the proportion of colloid being equivalent to 1 per cent of the product (Fig. 31). This process has also been developed to the manufacturing scale.

(c) Lead azide (R.D.1333). A modified form of lead azide has been developed in order to give a composition of improved cohesive properties on pressing. In this preparation solutions of lead acetate and sodium azide are added simultaneously to a stirred dilute solution of sodium carboxy methyl cellulose. The resultant product consists of irregularly shaped granules which processes well and gives a remarkably free-flowing composition (Fig. 32). Some examples of the first stages of crystal formation are shown in Figs. 33-36. As the proportion of colloid incorporated is less than 0.8 per cent a high state of purity is maintained in the product as shown by determinations of azide value which are considerably higher than for other forms of lead azide in use. This method of preparation of lead azide has been shown to possess advantages on the manufacturing scale.

(d) Lead dinitroresorcinate. Colloids have been employed with lead 2:4 and 4:6 dinitroresorcinate to improve flowing properties (granulation), to modify rates of burning and to eliminate the effects of impurities. A large number of different products are possible and some of these have been developed to manufacturing scale and adopted for Service use as priming or delay compositions (R.D.1305, R.D.1307, R.D.1308).

Example of lead dinitroresorcinate composition developed to manufacturing scale (R.D.1305)

R.D.1305 was developed to meet the requirement of a 1 millisecond delay in Fuze 255. It illustrates the use of two colloids in one process to give required flowing bulk density and burning properties of an explosive. The precipitation of normal lead 2:4 dinitroresorcinate to give a range of products of varying particle size by the addition of lead hydroxide suspension to dinitroresorcinal suspension without the incorporation of a colloid results in a steep burning time - particle size curve when plotted in the one millisecond region for the Fuze 255 requirement. Particle size can be controlled by concentration of reactants or more conveniently by adjustment of temperature of the precipitation.

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By the addition of sodium carboxy methyl cellulose to the lead hydroxide suspension a final product can be prepared which breaks up into granules on drying; at the same time the burning time - particle size curve becomes much flatter allowing a practicable control of burning time of the final product by adjustment of temperature over a convenient range on the plant.

Simultaneously methyl cellulose added to the dinitroresorcinal suspension increases the bulk density of the final product to within the specified range for mechanical filling requirements. Tables can therefore be compiled for the manufacturer showing the required temperature adjustment and proportion of methyl cellulose to be added in order to give required delay and bulk density respectively.

(5) Employment of a proportion of the explosive as a colloid

Crystallising substances prepared by precipitation from interacting solutions can be varied in particle size by adjustment of conditions in accordance with Von Wiemarn's rule. It follows that if practical conditions can be devised to prepare a proportion of the substance with particle size so much reduced as to give a gel-like or colloidal precipitate it may be possible to employ the substance itself instead of an additive colloid. This has the decided advantage for explosive use that no inert diluent is introduced.

As an example the acid salt of lead 4:6 dinitroresorcinate is usually precipitated in the form of acicular crystals with completely unsatisfactory flowing properties (Fig. 37). By selecting suitable conditions of temperature and concentration of reactants a proportion can be precipitated in gel-like form to give a free-flowing granulated product by direct precipitation as shown in Fig. 38. Mixtures of acid and basic salts may also be prepared in the same way (Figs. 39, 40).

A further example of direct precipitation to give spherical granules is shown in Fig. 41 (Lead 2:4 dinitroresorcinate).

(6) Deposition and surface treatment

(a) Granulation by precipitation of hydrophilic colloids. These methods may be described as two stage processes as they consist of the preliminary precipitation of the explosive (usually in a finely divided or otherwise unsatisfactory physical form) followed by a separate granulation operation.

The suspension of the explosive in a dilute solution of the colloid is vigorously stirred and by the alternative means of the addition of organic solvents or electrolytes or by raising or lowering the temperature the colloid is thrown out of solution and under favourable conditions will give a granulated product with the explosive. The optimum conditions have been found to be generally critical and one processing difficulty is a tendency for the product to cake on drying if excess colloid is used; extrusion to obtain granules of satisfactory size may be necessary.

An example is the use of sodium carboxy methyl cellulose to give a granulated product with lead 4:6 dinitroresorcinate by the addition of alcohol which flocculates the colloid Fig. 42. Attempts have been made to dispense with the organic solvent by utilising the property of methyl celluloses of being more insoluble at higher temperatures; for example the explosive suspended in a dilute solution of methyl cellulose is stirred and heated above the coagulation temperature to precipitate the colloid. On cooling, the outer layer of methyl cellulose goes into solution thus avoiding caking on the product on drying. Such a method has advantages over the use of electrolytes for salting out the hydrophilic colloid on account of possible reactivity and absorption at the concentrations required.

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(b) Precipitation of insoluble materials and surface treatment. The co-precipitation and surface deposition of insoluble substances represent further stages in modifying explosives not only to eliminate mechanical mixing but also to impart new properties. For example an insoluble material can be introduced in the precipitation of the explosive usually in conjunction with the use of a hydrophilic colloid as described in (4) above. The insoluble material is employed in a very finely divided state preferably suspended as a hydrophobic solution. Fig. 43 is an example of a hydrophobic sol (colloidal graphite) incorporated during the precipitation of a granular explosive (lead styphnate) in the presence of a hydrophilic colloid (methyl cellulose); this is a single stage process starting from the solutions required for the double decomposition and the two colloids.

Another method is to prepare the insoluble material in a finely divided condition by ball milling or alternatively by the use of a colloid mill and a proportion of protective hydrophilic colloid and depositing on the surface of the preformed explosive; this is of course a two stage process. Substances available commercially as hydrophobic sol suspensions may be used directly as in the case of colloidal graphite. Various methods have been investigated and employed for securing satisfactory deposition including the wider use of lyophobic sols in media other than water. Fig. 44 shows graphite deposited on lead styphnate to give a conducting composition which unlike the untreated explosive can only be ignited by electric sparks of extremely high energy.

Reproductions of mechanical mixtures to give homogeneous non-segregating compositions have been made by similar precipitation methods and examples could include antimony sulphide - mercury fulminate, aluminium-lead styphnate and the incorporation of stearates of metals. In addition to replacement of mixtures this field has been shown to give opportunities for improving electrostatic properties, burning and flash characteristics (e.g. introduction of "hot particles" in a finely divided and evenly distributed manner), elimination of pressing difficulties by incorporating a lubricant and the application of insensitive coatings and coatings to improve compatibility and stability of the composition. Water repellent films have been applied to crystalline product during manufacture to improve stability.

A special aspect of surface treatment and co-precipitation is the improvement in flowing properties which may be obtained by including small quantities of suitable substances to reduce surface friction; this is a further or alternative stage to modifying particle size and shape. The excellent flowing properties of lead azide R.D.1333 despite the irregular contour of the particles may be attributed to reduction of friction by a surface film of lead carboxy methyl cellulose.

An example of a non-segregating granular composite mixture of lead azide and PETN is shown in Fig. 45 and the structure of the granule is seen in Fig. 46 a combination X-ray light photograph. This was prepared using lead carboxy methyl cellulose as the binding agent.

Attention has been given to precipitating a less sensitive explosive on to a sensitive initiator in order to increase safety during handling. On loading the composite granule breaks down giving a uniform mixture of the components. For example barium styphnate has been precipitated over lead styphnate.



## Conclusions

(1) The results described prove that a very large number of products of different physical and explosive properties can be prepared from a small number of explosives. This is particularly important as there are relatively few substances which combine initiating, priming or fast burning characteristics with adequate stability. It is therefore necessary to employ all possible means of modification of properties particularly those methods of preparation which have been shown to be readily applicable on the production scale. For example, it has been demonstrated with lead styphnate that the one explosive can be used as the basis of manufacturing processes giving (a) a free-flowing product consisting of crystals narrowly controlled to habit and size with high apparent bulk density/density ratio (application as an ingredient for detonating and cap compositions), (b) a product of selected crystal habit and size to give a non-segregating mixture with a less dense component (application for electrically fired caps) and (c) a product consisting of rounded granules by direct precipitation possessing quite different explosive properties (fast delay composition). In addition lead styphnate has been modified by deposition of a surface coating to render it virtually insensitive to ignition by electric sparks of high energy; untreated the same crystalline material is extremely sensitive to this form of ignition. Other experiments have given further modifications of the same explosive including a granular form incorporating a lubricant, an alternative granulated detonating composition, and a polymorphic form of possible application to Service use.

(2) Much of the experimental work has been devoted to precipitation in the presence of additive substances or impurities. The examples given in this report include crystallisation in the presence of impurities during transition of the main substance. Such changes have been representative of polymorphic transition (e.g. beta to alpha lead azide); transition from salts of different basicity (e.g. acid to basic salts of lead 4:6 dinitroresorcinato); transition from higher to lower hydrates (e.g. trihydrated to monohydrated barium styphnate).

This indicates sensitiveness to such changes and can afford a guide to the selection of conditions for the most effective control of crystallisation by additive substances. This phenomenon has been known and previously remarked in the literature (Hedvall Chem. Reviews 15 139, 1934) and the examples described in this report provide further experimental evidence. It is evident however that such transitions are not always essential for effective co-precipitation. For instance the precipitation of lead styphnate in the presence of methyl cellulose on the plant scale has given opportunities of obtaining samples during the early stages of crystallisation and examining by X-ray diffraction for evidence of polymorphic or other transition. No substance other than the alpha normal monohydrate has been found although lead styphnate can form a polymorph, a basic salt or a complex salt under suitable conditions.

(3) The frequent use of methyl cellulose and derivatives as co-precipitants may be noted in the examples. Although other types of colloids have been studied it is evident that the cellulose ethers and esters (and also some corresponding starch derivatives) are particularly effective; they may be employed successfully in small proportions to modify crystal shape very markedly without diluting desirable explosive properties. The single spherical crystal of barium styphnate may be compared in its formation with corresponding polycrystalline granules of other explosives. When the complex nature of these crystallisations is considered together with the relatively slow rate of precipitation the uniformity of development of the final particles is remarkable; for example the early states of formation of granulated lead azide can show a wide range of phenomena including nucleation within gel fragments yet the product, is free from fragments and oversize aggregations.



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In the use of the glycollates as co-precipitants (e.g. lead azide precipitated in the presence of sodium cellulose glycollate, R.D.1333) it should be noted that in many cases the effective co-precipitating colloid is the insoluble metal salt of the glycollic acid. This is important because the heavy metal salts can impart moisture repellent properties; thus the final co-precipitated explosive can be expected to have greater moisture resistance than if prepared by precipitation in the presence of a hydrophilic colloid without salt forming properties.

(4) The development of the methods given has provided increasing evidence that the objective of crystals approaching spherical shape to obtain optimum flowing properties should be accepted with some reservation. It is shown that a very irregularly shaped particle can possess very good flowing properties. The surface condition of the crystal may, in practice, be of greater importance than the shape in the development of a suitable method of preparation of a new composition.

(5) It is considered that the results emphasize the possibilities of using very small amounts of additive substances to secure substantial improvement in crystallisation. This is shown particularly with the non-ionic surface active agents e.g. with lead azide.

(6) The use of surface-treatment and deposition on crystals to modify physical properties has received considerable attention in this work and the examples are indicative of a number of interesting experimental products which have been prepared.

#### Recommendations

(1) The results described have been based directly upon the necessity of meeting Service and experimental requirements with the explosives available. For long term investigations on crystallisation it may be advantageous to include the study of substances, not necessarily of explosives application, which would broaden the basis of methods for modifying physical properties. Satisfactory initiatory explosives may be regarded as unrepresentative, possessing special properties such as adequate chemical stability combined with certain degree of instability to heat or shock. Where crystallisation phenomena of value have been obtained with an initiator it would be of interest to determine if the results can be repeated with substances related chemically and crystallographically. Conversely more general information on the modification of crystals of related substances may directly assist in obtaining desired results with an explosive.

(2) Continued investigations should include further attention to the employment of both non-ionic and ionic surface active agents. In addition to the use of water soluble or dispersible types to control crystal nucleation and growth those soluble in organic solvents have application in connection with improvement in flowing properties and treatment to improve stability.

(3) The methods described for surface treatment, deposition, and co-precipitation afford means of replacing mechanical mixtures by wet-precipitated non-segregating compositions. This eliminates both the necessity for the dry mixing of very sensitive explosives and the possibility of segregation of components on handling and resulting failure in use. Only a very small beginning has been made to replace the many complex mechanical mixtures now in use and consideration of further application of these methods appears to be justified.

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References (previous reports)

General	C.R.D.D. 1/M/47
Lead azide	A.R.D. Expl. Report No. 607/46
Lead styphnate	A.R.D. Expl. Report No. 281/45
	" " " No. 286/45
	" " " No. 612/46
	E.R.D.E. Report No. 17/R/48
Lead dinitroresorcinate	A.R.D. Expl. Report No. 575/44
	" " " No. 680/44
	" " " No. 282/45
	" " " No. 608/46
	E.R.D.E. Report No. 10/R/48
	" " " 11/R/48
Barium styphnate	A.R.D. Expl. Report No. 569/44
	" " " No. 602/46

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Fig1. X50  
Barium styphnate from barium acetate  
and styphnic acid



Fig.2. X50  
Barium styphnate from barium chloride  
added to magnesium styphnate.

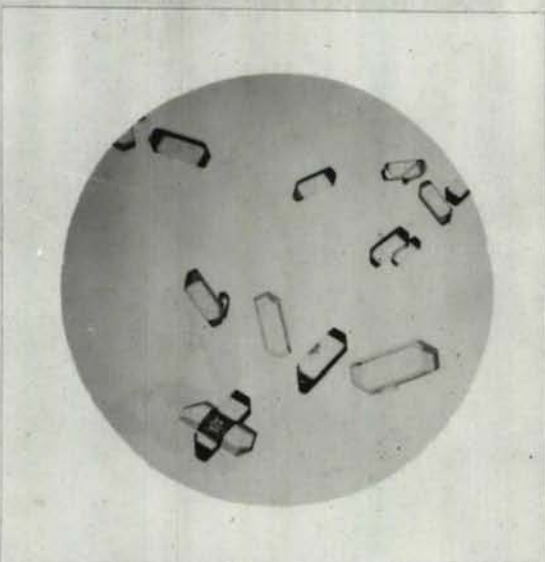


Fig3. X50  
Barium styphnate from magnesium  
styphnate added to barium chloride.

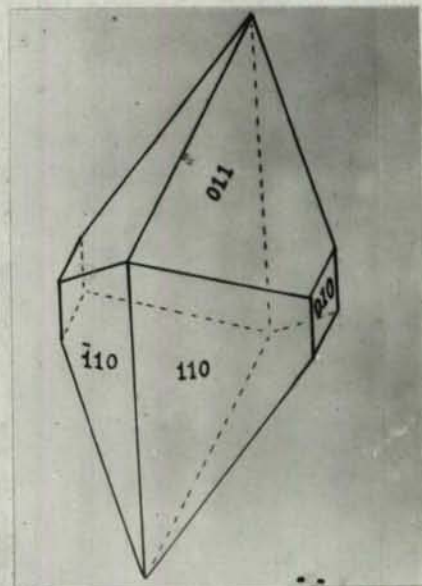


Fig4.  
Barium styphnate crystal  
habit of RD1320

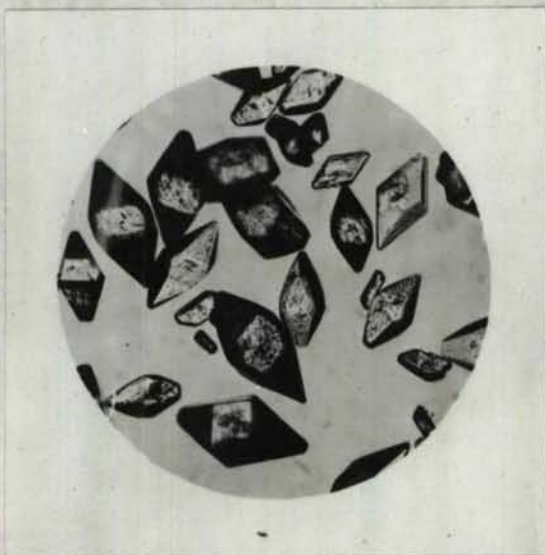


Fig5. X50  
Barium styphnate crystals RD1320



Fig6. X50  
Barium styphnate trihydrate (accicular)  
being converted to fig.5 product  
(monohydrate).



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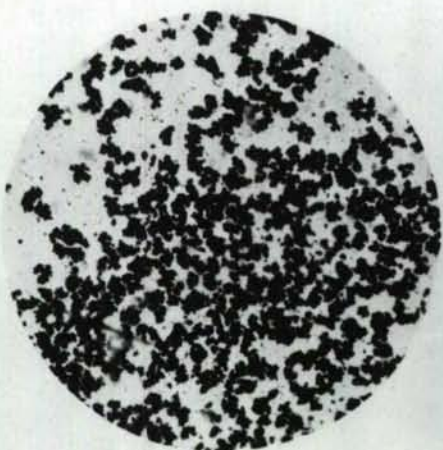


Fig 7. X50  
Lead styphnate intermediate opaque  
microaggregates complex

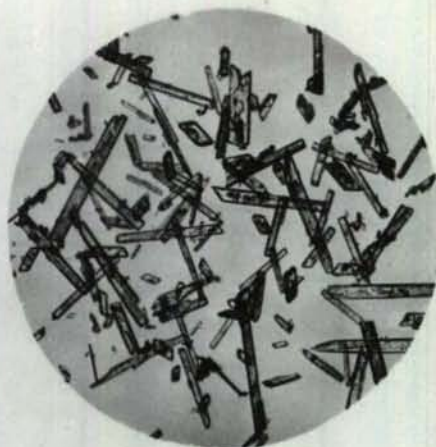


Fig 8. X50  
Lead styphnate intermediate, lead  
aceto-styphnate

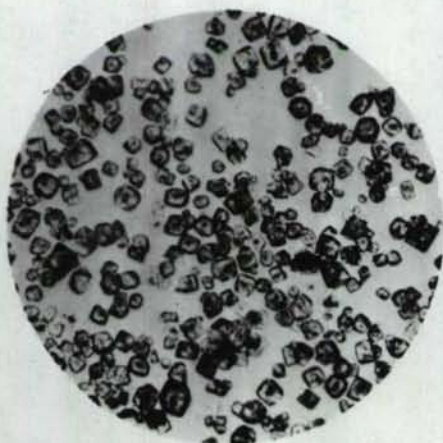


Fig 9. X50  
Lead styphnate, equant habit,  
RD1302

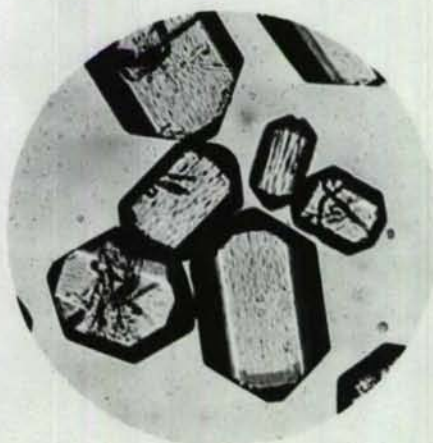


Fig 10. X200  
Lead styphnate, tabular habit

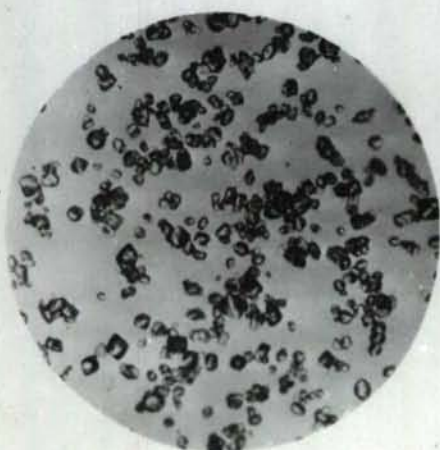


Fig 11. X100  
Lead styphnate RD1303.

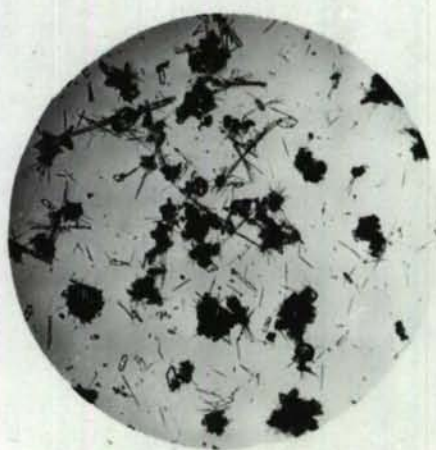


Fig 12. X50  
Lead styphnate RD1302 intermediate  
stage after 3mins. addition of nitric acid

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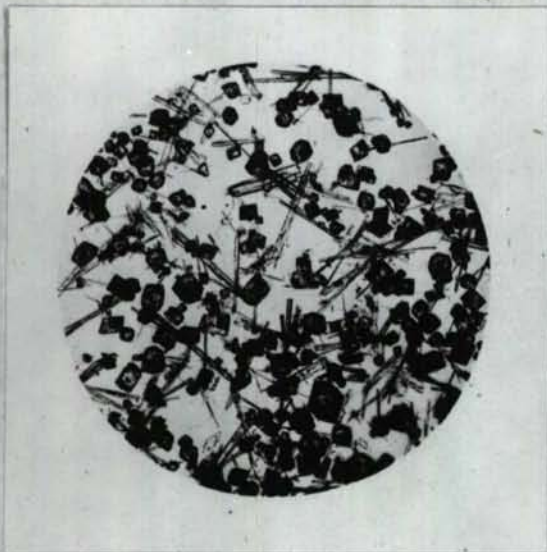


Fig13. X50  
Lead styphnate RD1302 intermediate stage after 5mins. addition of nitric acid

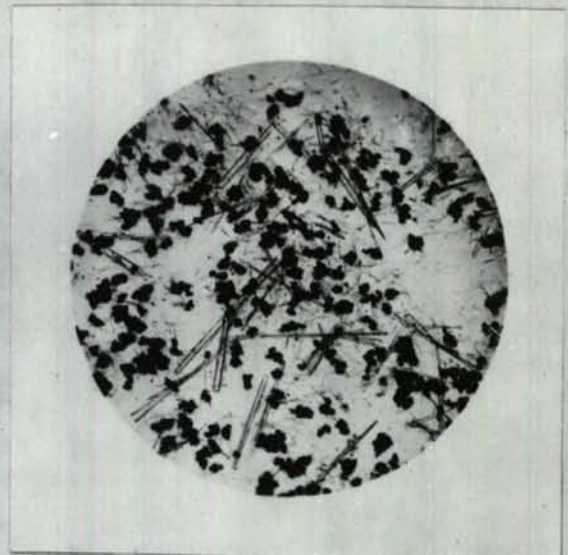


Fig14. X50  
Lead styphnate RD1303 intermediate stage after 7mins.

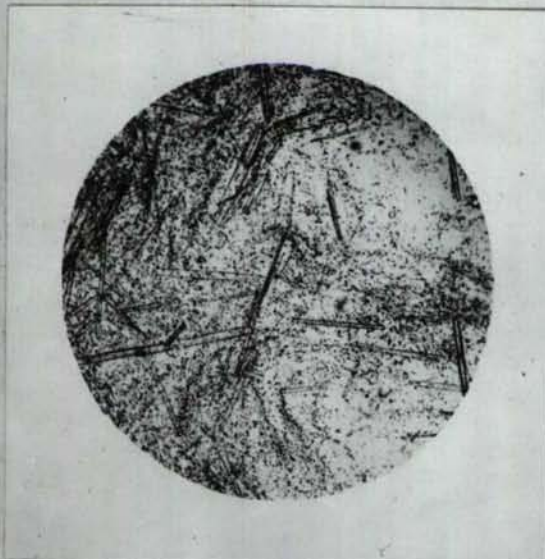


Fig15. X50  
Lead styphnate RD1303 intermediate stage after 9mins.

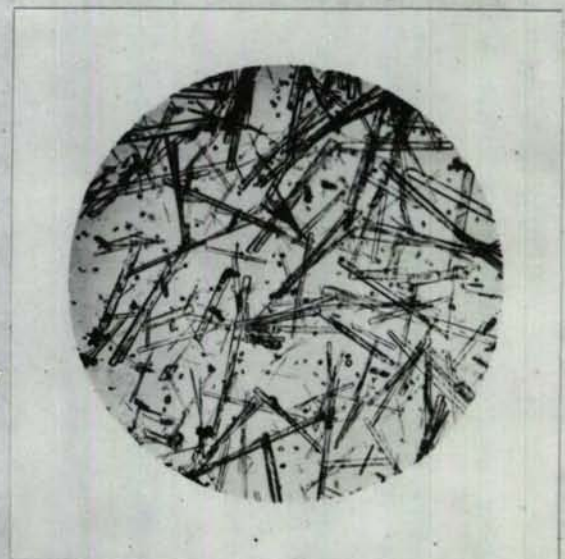


Fig.16. X50  
Lead styphnate RD1303 intermediate stage after 10mins (1min of nitric acid addition)

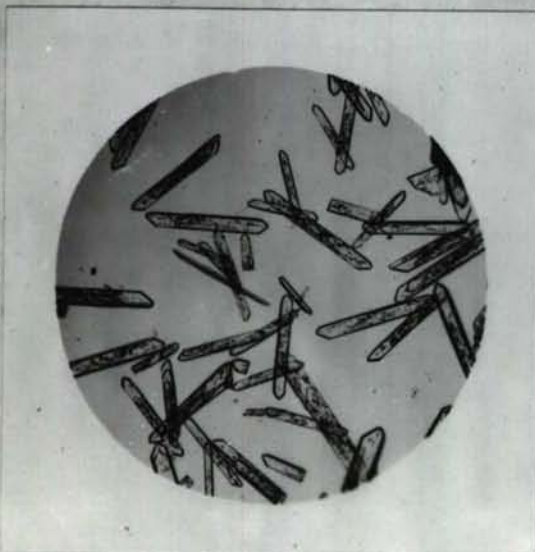


Fig17. X50  
Barium styphnate precipitated in presence of methyl cellulose

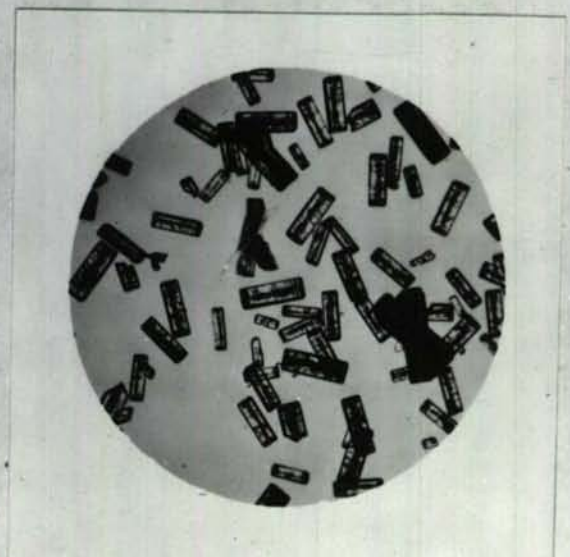


Fig 18. X30  
Barium styphnate precipitated in presence of sodium carbonate and carboxy methyl cellulose

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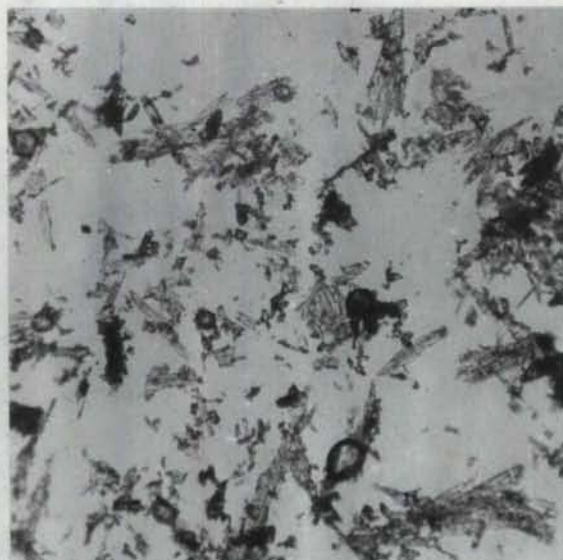


Fig 19  
Control, no addition, 5mins

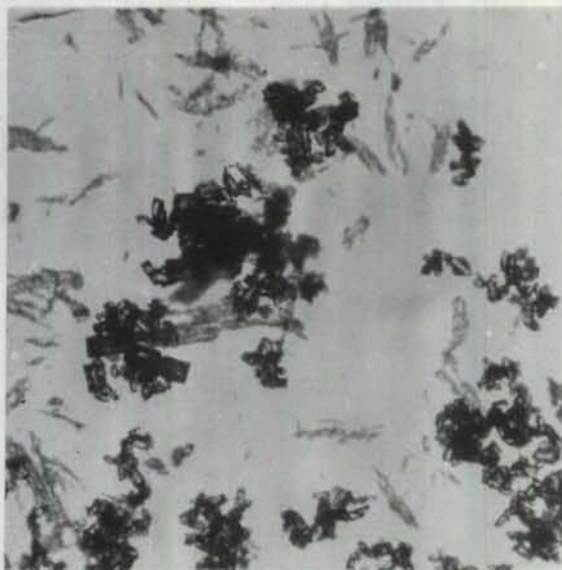


Fig 20  
Control, 10mins, end of precipitation



Fig 21  
Addition of water dispersed non-ionic  
surface active agent, 5mins.

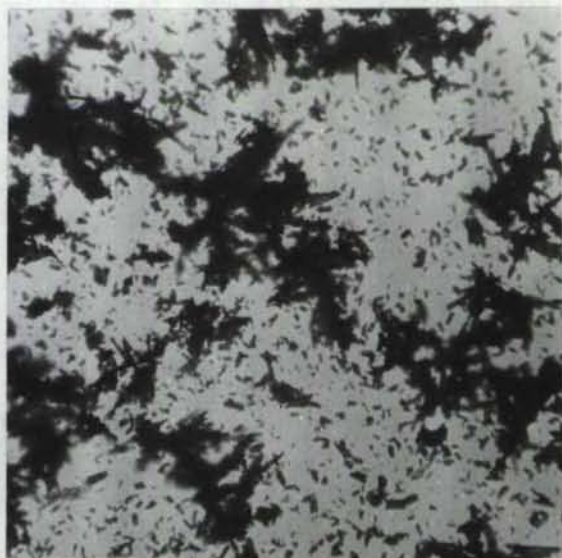


Fig 22  
Addition of water dispersed non-ionic  
surface active agent, 10mins, end of pptn.



Fig 23  
Addition of water soluble non-ionic surface  
active agent, 5mins.

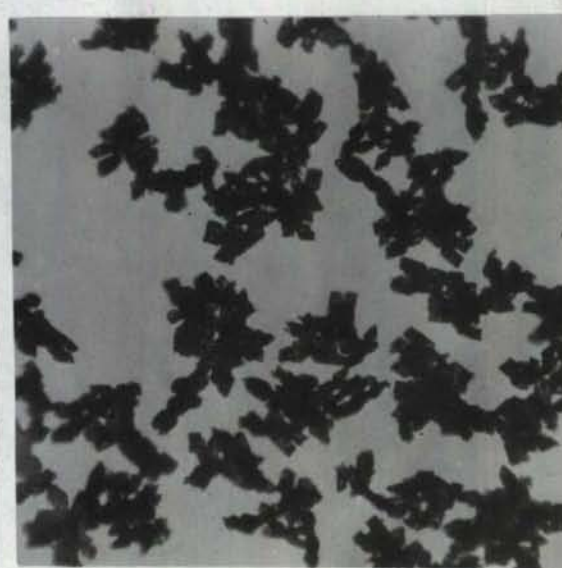


Fig 24  
Addition of water soluble non-ionic surface  
active agent, 10mins, end of pptn.

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Fig. 25 X50  
Lead azide precipitated in the presence of sulphate type of surface active agent.



Fig. 26 X500  
Lead azide, service, showing nucleating growths of lead carbonate

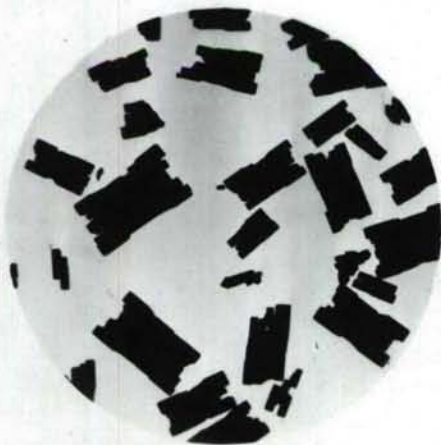


Fig. 27 X60  
Lead azide co-precipitated with colloidal graphite.

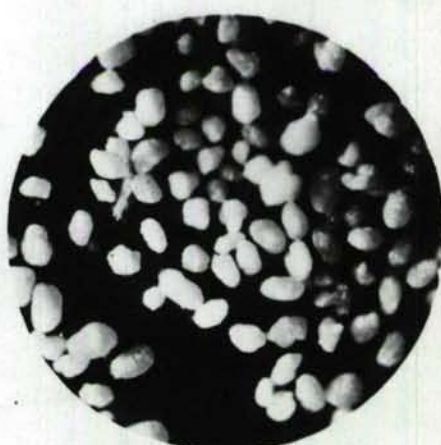


Fig. 28 X25  
Barium styphnate granulated, precipitated with 0.7% sodium carboxy methyl cellulose

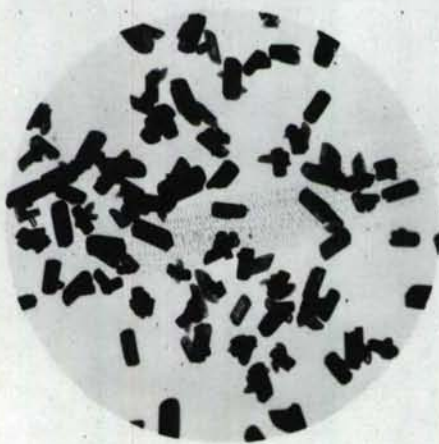


Fig. 29 X25  
Barium styphnate precipitated with 0.5% sodium carboxy methyl cellulose

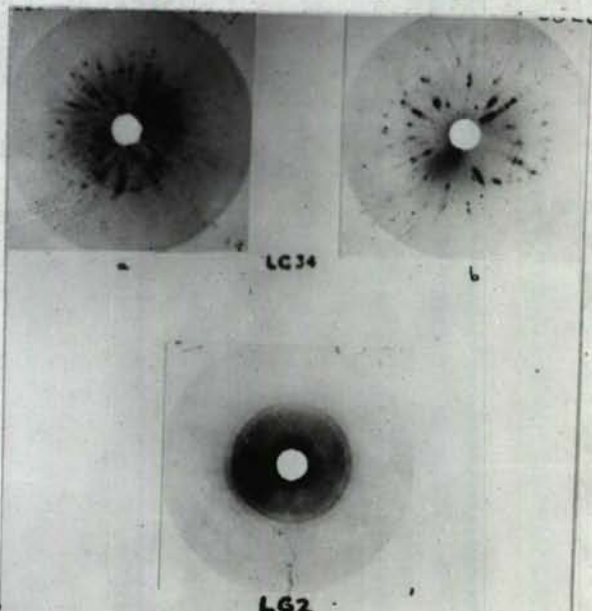


Fig. 30.  
X ray diffraction photographs of barium styphnate  
LG34, a, b, of product as fig. 28  
LG2 with increased proportion of sodium carboxy methyl cellulose

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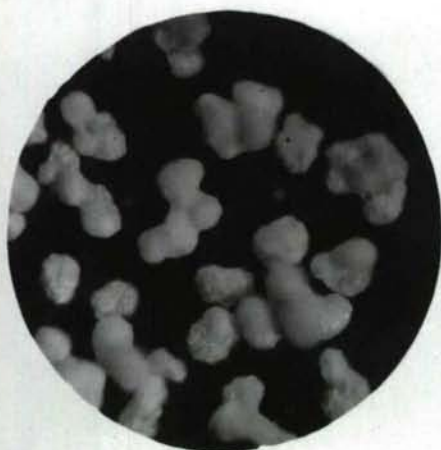


Fig 31 X50  
Lead styphnate precipitated with  
methyl cellulose



Fig 32 X50  
Lead azide co-precipitated with  
sodium carboxy methyl cellulose (RD1333)

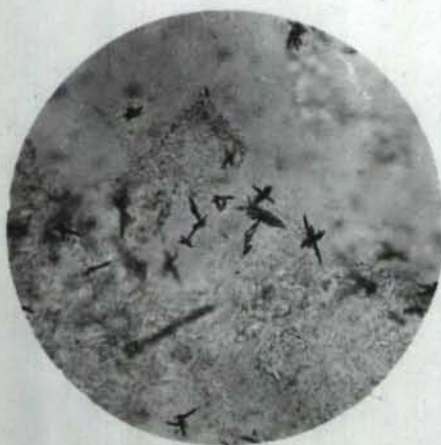


Fig 33 X50  
Lead azide RD1333. Early formation of  
granules in gel fragments of lead  
carboxy methyl cellulose

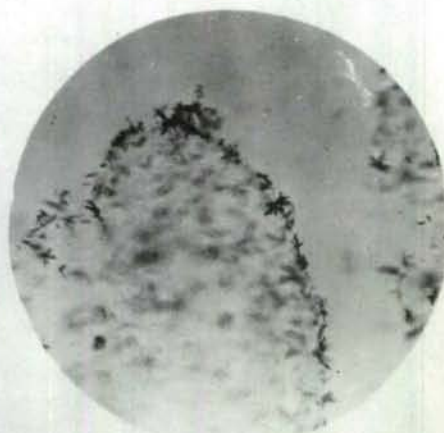


Fig 34 X50  
Lead azide RD1333. Early formation of  
granules on surface of gel fragments

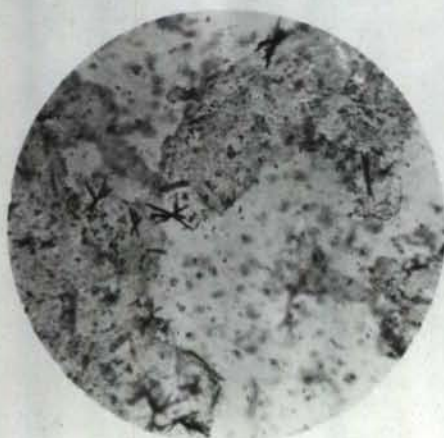


Fig 35 X50  
Lead azide RD1333. First appearance  
of  $\alpha$  dendrites

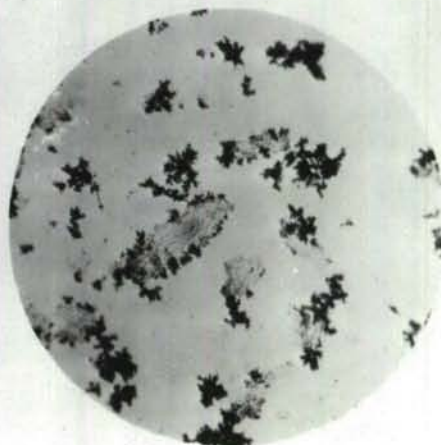


Fig 36 X50  
Lead azide RD1333 Experimental nucleation  
showing formation of  $\alpha$  crystals on surface  
of large  $\beta$  crystals



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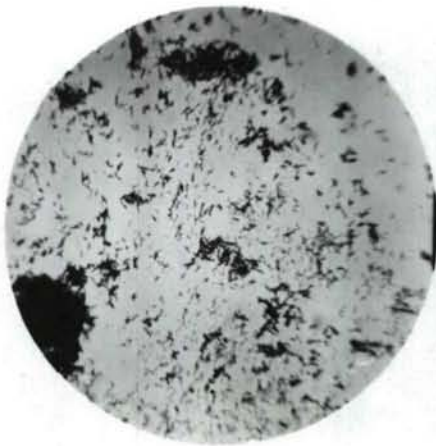


Fig 37 X25  
Lead 4:6 dinitroresorcinate. Acid  
salt Pb = 34 %

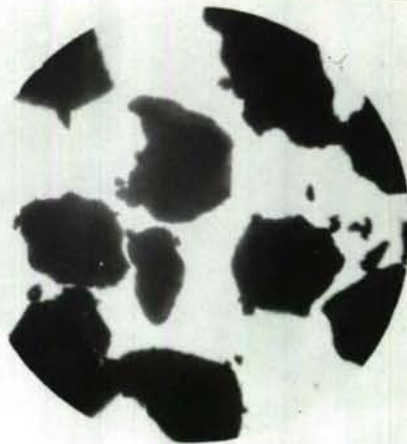


Fig 38 X25  
Lead 4:6 dinitroresorcinate Acid  
salt self-granulated Pb = 34 %

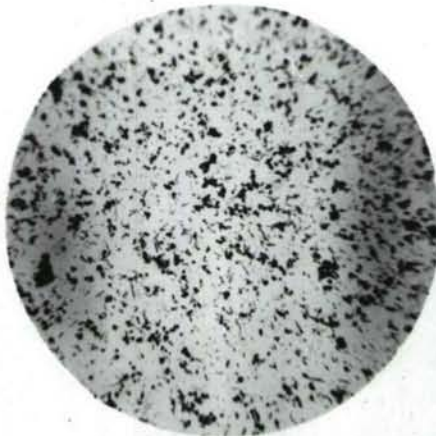


Fig 39 X25  
Lead 4:6 dinitroresorcinate. Service  
L.D.N.R. Pb = 61.1 %

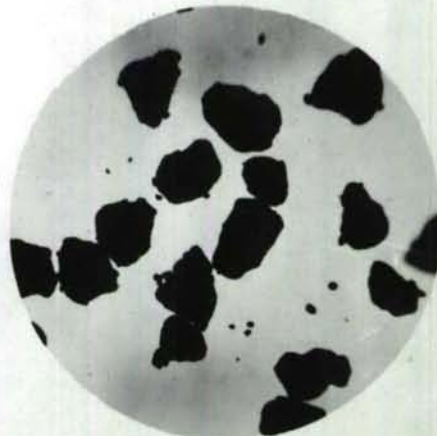


Fig 40 X25  
Lead 4:6 dinitroresorcinate  
self granulated Pb = 61.9 %

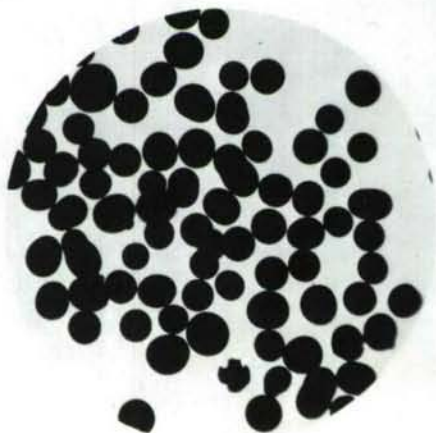


Fig 41 X60  
Lead 2:4 dinitroresorcinate granulated  
by direct precipitation

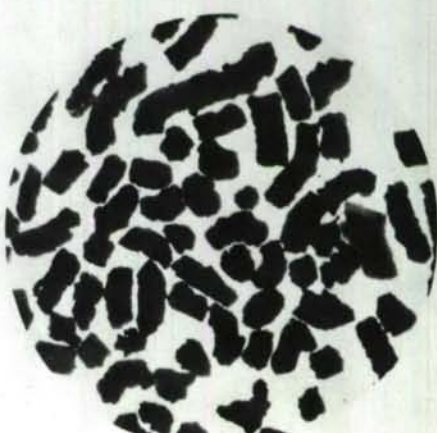


Fig 42 X10  
Lead 4:6 dinitroresorcinate granulated  
with carboxy methyl cellulose

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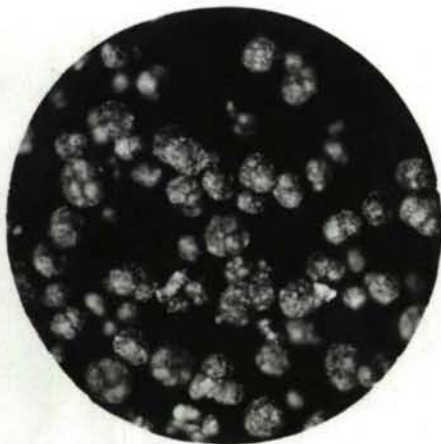


Fig 43. X50  
Lead styphnate, granulated, co-precipitated with colloidal graphite



Fig 44. X280  
Lead styphnate, graphite surface deposited.

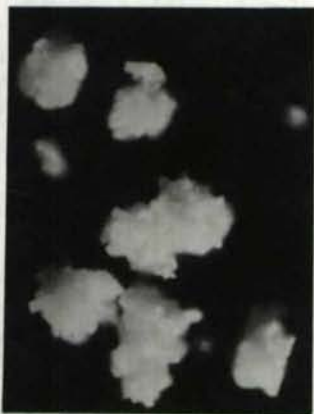


Fig 45 X50  
Lead azide - P.E.T.N. Composite granule

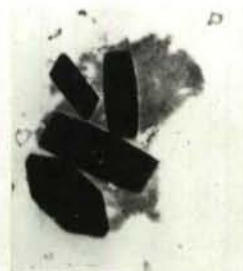


Fig 46 X150  
As fig. 45 combination  
Xray light photograph

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